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Reprinted from J. Phys. Chem. Solids
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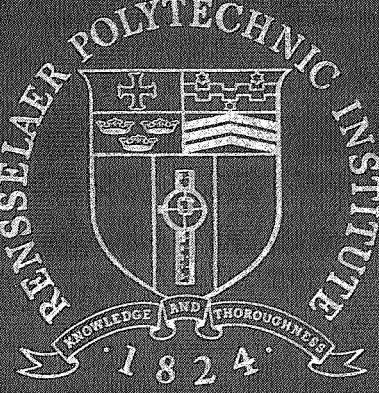

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J. Phys. Chem. Solids Pergamon Press 1969. Vol. 30, pp. 367–373. Printed in Great Britain.

THE DEBYE–WALLER FACTOR. DEBYE TEMPERATURE FOR NICKEL*

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(*Received* 17 *May* 1968; *in revised form* 28 *June* 1968)

Abstract—Three Born–von Kármán lattice dynamical models obtained from neutron measurements and elastic constant measurements on Ni have been considered chiefly to calculate the Debye–Waller factor Debye temperature, $\theta^M(T)$. The results are compared with X-ray experimental data in the region 100°K $\leq T \leq$ 520°K. Also considered are the dispersion curves, the moments of the frequency spectrum and the dependence of these moments upon the temperature. It is seen that for $\theta^M(T =$ 296°K), the models based on the neutron data yield 403° and 406°K, the model based on the elastic constant data yields 425°K, and the X-ray experimental value is 410°K. It appears that at high temperatures the temperature dependence of $\theta^M(T)$ determined using the model based on the elastic constant data agrees closely with experiment whereas the temperature dependence of $\theta^M(T)$ determined from thermal expansion effects alone is too small by a factor of two. However, due to experimental scatter, it is possible that only volume expansion effects are important in determining the temperature dependence of $\theta^M(T)$ at high temperatures.

1. INTRODUCTION

THE Debye–Waller factor Debye temperature, $\theta^M(T)$, for Ni, has been determined[1] by X-ray relative intensity measurements in the region 100°K $\leq T \leq$ 520°K. Wilson[1] interpreted the data with the use of a continuum model based on the measured elastic constants [2]. In this paper[3] results of calculations of $\theta^M(T)$ for Ni based on simple Born–von Kármán lattice dynamical models are presented and the comparison between theory and experiment is shown. Several studies of $\theta^M(T)$, based on the use of force models or on analyses of thermodynamic data have appeared in the literature for other substances [4, 5]. We used a fourth nearest neighbor Begbie–Born model, a fifth nearest neighbor axially symmetrical model, and a first nearest neighbor Begbie–Born model. The force constants of the latter model were determined from available elastic constant data[2] in the usual way[6–8]. Hopefully, anharmonic or electron–phonon interaction effects in the Debye–Waller factor are accounted for in an approximate way by the inclusion of the temperature dependences of the elastic constants and equilibrium volume[9] in determining the harmonic force constants. It should also be pointed out that the elastic constant measurements were performed in the presence of a magnetic field. The force constants given by Birgeneau *et al.*[10] were used for the remaining models, which are based on the neutron data of Birgeneau *et al.* at $T = 296$°K[10]. Birgeneau *et al.* presented results of calculations of the frequency spectrum, the specific heat Debye temperature and several moments of the frequency spectrum for the fourth neighbor model.

A recent calculation[11], on the basis of the Birgeneau *et al.* fourth neighbor model, of the Debye–Waller factor for nickel at $T = 300$°K has been brought to the author's attention by the referee. In their calculation Barron and Smith use 1000 phonons in the Brillouin zone and an integration over 1/1000th of the Brillouin zone with an approximation for the long wavelength modes.

*This work was supported in part by the National Aeronautics and Space Administration through the Rensselaer Polytechnic Institute Interdisciplinary Materials Research Center, and the Army Research Office (Durham).

In addition, Gleiss[12] has calculated the Mössabuer fraction for nickel at temperatures less than 200°K. Most of Gleiss's calculations are based on the moments of the frequency spectrum with the use of high and low temperature expansions. He used moments for the Birgeneau *et al.* fourth nearest neighbor model and moments which he obtained from an analysis of the thermodynamic data. Gleiss also considered a second nearest neighbor model based on elastic constant data and he compared his results with Mössbauer measurements[13]. We believe that our calculations constitute a significant improvement over previous work on the Debye–Waller factor for nickel because our method of calculation (to be discussed) appears to be more exact than the methods used by Barron and Smith and by Gleiss, and because our calculations involve a few models, including the Birgeneau *et al.* fifth neighbor model (not considered in previous studies) and a wide range of temperatures.

In the harmonic or quasi-harmonic approximation $\theta^M(T)$ for a cubic monatomic crystal is given by

$$\sum_{\vec{f},j} \frac{e_{vib}(\omega, T)}{\omega^2} = \frac{9N\hbar^2}{kTx}\left[\frac{1}{4}+\frac{1}{x^2}\int_0^x \frac{x'dx'}{e^{x'}-1}\right] \quad (1)$$

where $x = \theta^M/T$ and where $e_{vib}(\omega, T)$ is the contribution to the vibrational energy of the mode of frequency ω and of wave vector and polarization index $\vec{f}$ and j, respectively. Although the left hand side of (1) can be evaluated with the use of a calculated frequency distribution[14], the normal mode sums discussed in this paper were performed directly over a cubic grid of 2992 points in the irreducible element of the Brillouin zone.

In order to make further comparison among the various models, the dispersion curves and the moments of the frequency distribution at $T = 296$°K were also considered. The moments of the frequency distribution are expressed in terms of an effective Debye frequency[15] or, equivalently, an effective Debye temperature,

$$\theta_D(n) = \frac{\hbar}{k}\{\tfrac{1}{3}(n+3)\langle\omega^n\rangle\}^{1/n} \quad (2)$$

where $\langle\omega^n\rangle$ is the n'th moment of the frequency distribution and where the limit of the right hand side of (2) is taken for $n = -3$ and for $n = 0$. We note that for values of n of -3, 2, -1, -2, and 0, $\theta_D(n) = \theta_0^c$, θ_∞^c, θ_0^M, θ_∞^M, and θ_∞^s, respectively. The superscripts c and s denote specific heat and entropy, respectively, and the subscripts refer to limiting temperatures.

2. RESULTS

The dispersion curves for the symmetry directions are shown in Fig. 1 for the first neighbor Begbie–Born model. The elastic constants at $T = 300$°K were used. The small disagreement between theory and experiment in the long wavelength region represents a discrepancy between elastic constant measurements and neutron measurements which has been noted previously[10, 16] and which is of theoretical interest[16]. Results for the Birgeneau *et al.* models, which were fitted to the experimental data points to within about 2 per cent, are not shown in the figure.

In Fig. 2 the comparison between the Barron Plots, i.e. $\theta_D(n)$ vs. n, is shown for the three models considered in this paper at room temperature. The values of $\theta_D(-3)$ were obtained with the use of de Launay's tables.* The calculations were performed at intervals of n of 0·5 and 1 depending on the range of n. The deviations of the values of $\theta_D(-2{\cdot}5)$ from the respective $\theta_D(n)$ curves are believed to be due to the crudeness of the grid size for calculating $\theta_D(n)$ near $n = -3$. The estimated errors in $\Theta_D(n \geq -z)$ and $\Theta^M(T)$, due to the grid size, are less than 2°K.

The calculated values of $\theta^M(T)$ for the fourth and first neighbor models are compared with experiment in Fig. 3. The minimum temperature interval for which the calculations

*We agree with the elastic constant value of Alers *et al.* of $\theta_0^c = 476$°K given in their *Bull. Am. Phys. Soc.* paper.

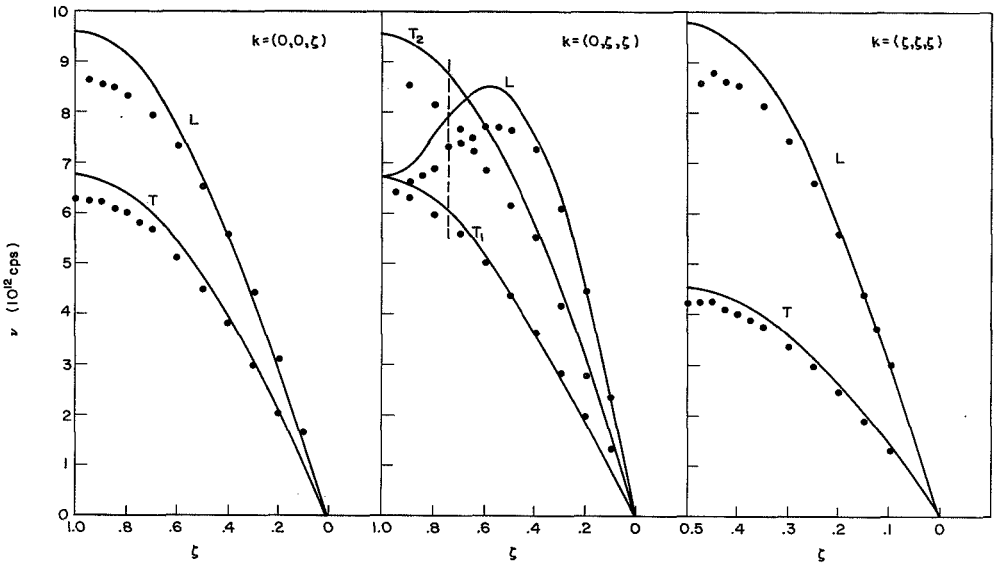

Fig. 1. Dispersion curves for Ni at $T = 296°K$. L and T refer to the longitudinal and transverse branches. The circles correspond to the neutron measurements of Birgeneau *et al.* (reference [10]), the solid lines correspond to the Begbie–Born first nearest neighbor model and the dashed vertical line corresponds to the Brillouin zone boundary.

were performed was 20°K and was in the region $0 \leq T \leq 100°K$. The effect of thermal expansion on $\theta^M(T)$, as shown in the figure, was obtained with the use of the approximate relation[18].

$$\frac{\Delta\theta^M}{\theta^M} = -\gamma\frac{\Delta V}{V} \tag{3}$$

where γ is the Gruneisen parameter and where $\Delta\theta^M$ and ΔV are the shifts in the Debye–Waller factor Debye temperature and equilibrium volume from their values at $T = 296°K$. It was assumed that $\gamma = 2$ at all temperatures and the thermal expansion data of Nix and McNair[9] for $\Delta V/V$ was used. It should also be noted that the $\theta^M(T)$ curve for the fifth neighbor model lies less than 1 per cent above the $\theta^M(T)$ curve for the fourth neighbor model.

3. DISCUSSION

Three Born–von Kármán force models for nickel have been considered chiefly to calculate $\theta^M(T)$, the effective Debye–Waller factor Debye temperature, and the results have been compared with experiment. Two of these models were proposed by Birgeneau *et al.* on the basis of their neutron data at $T = 296°K$[10]. The other model is the Begbie–Born first neighbor model which has been considered on the basis of the elastic constant data of Alers *et al.*[2]. The model which yields results in best agreement (less than 1 per cent) with the quoted experimental value of $\theta^M = (410 \pm 10)°K$ at room temperature is the fifth neighbor axially symmetrical model considered by Birgeneau *et al.* However, the difference in $\theta^M(T)$ between the two Birgeneau *et al.* models is less than 1 per cent which may be of the order of the error in $\theta^M(T)$ for either model due to uncertainties in the neutron data. The first neighbor model yields a result for θ^M at room temperature which is about 5 per cent above the respective Birgeneau *et al.* models and the quoted experimental value. It should be pointed out that all three models agree with the quoted experimental value for θ^M at room temperature to within the accuracy of the

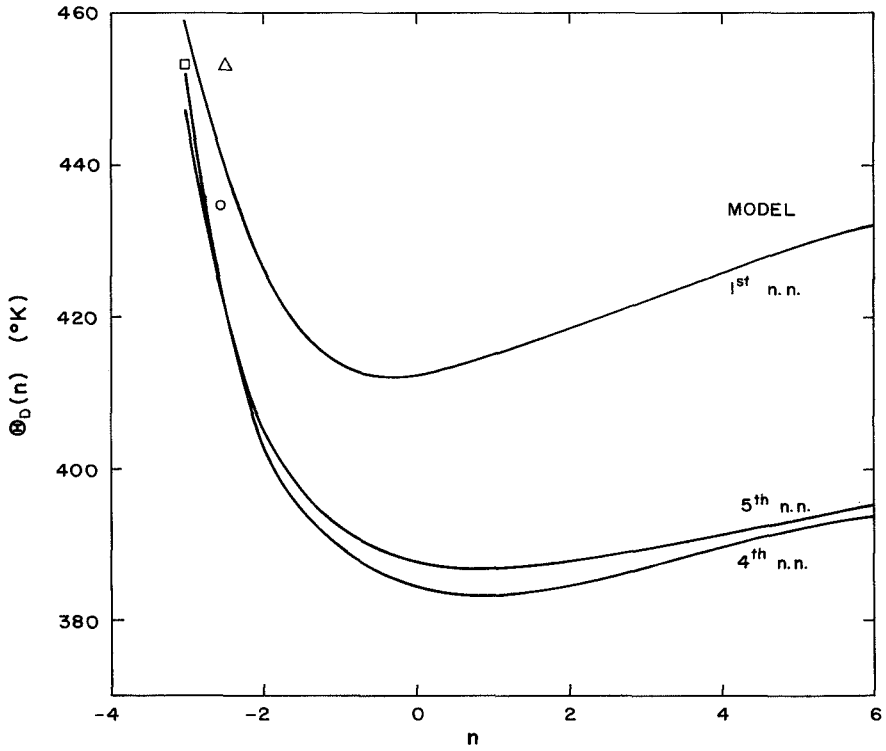

Fig. 2. Barron plots for Ni at $T = 296$°K calculated from the three force models considered in the text. $\theta_D(-3)$ was calculated using de Launay's tables whereas other values of $\theta_D(n)$ were calculated using a cubic grid of 2,992 points in 1/48 of the Brillouin zone. The square refers to $\theta_D(-3)$ calculated from Bozorth *et al.*'s elastic constant measurements (reference [17]) and the circle and triangle refer to $\theta_D(-2{\cdot}5)$ calculated for the fourth and first nearest neighbour models, respectively. The fourth and fifth *n.n.* models cross between $n = -2$ and $n = -3$.

latter value which is limited by experimental error and by the method[1] of determining $\theta^M(T)$ from the data. However, as suggested by the investigation of Birgeneau *et al.*, it is seen that the first neighbor model is inadequate for representing the measured dispersion curves.

Our results can easily be compared with the calculation of Barron and Smith[11] and with the experimental results of Inkinen and Suortti (see Barron and Smith for reference) at $T = 300$°K. Barron and Smith considered the coefficient B of $\sin^2\theta/\lambda^2$ in the Debye-Waller factor. They report $B = 0{\cdot}381 \pm 0{\cdot}008$ Å^2 for the calculated value and $B = 0{\cdot}37 \pm 0{\cdot}02$ Å^2 for the experimental value. The value $\pm 0{\cdot}008$ Å^2 is due to uncertainties in the neutron data. We obtain $B = 0{\cdot}377$ Å^2 for the fourth neighbor model, which is in good agreement with Barron and Smith's value, and $B = 0{\cdot}372$ Å^2 for the fifth neighbor model.

The effect of thermal expansion on $\theta^M(T)$ has been treated approximately. The justification of this treatment is suggested by the experimental information on the temperature dependence of the Gruneisen parameter for Ni[19] and reference is made to previous papers[5, 20, 21] for a more detailed discussion of thermal expansion effects. It is hoped that the first neighbor Begbie-Born model provides an estimate of the full anharmonic effect in $\theta^M(T)$ although the theory may not be justifiable. A more exact treatment of the anharmonic effect is avail-

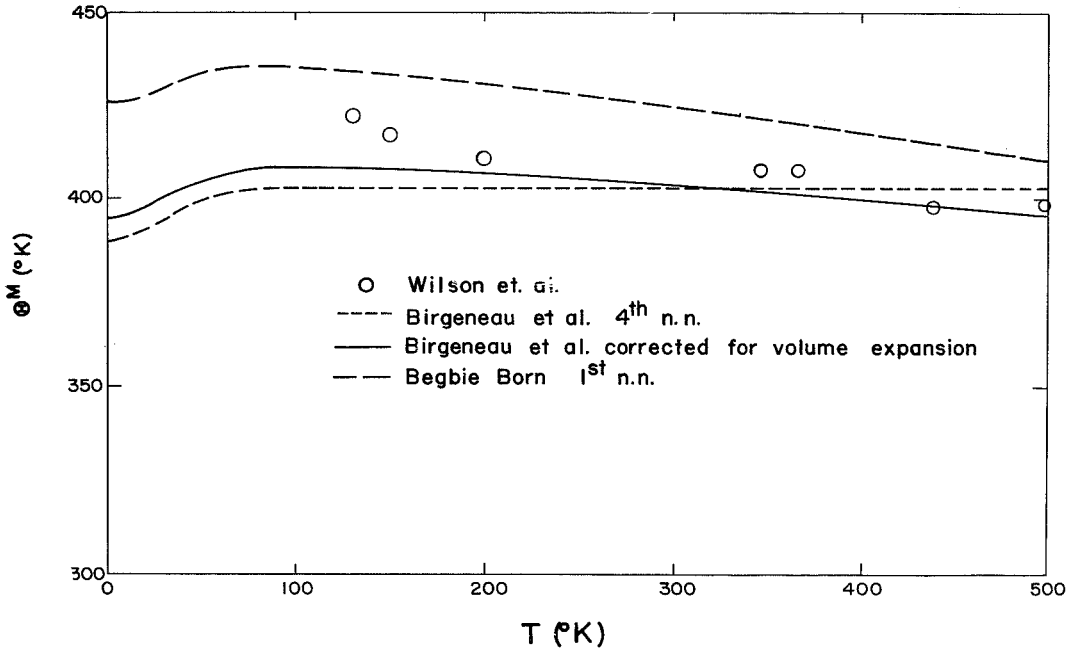

Fig. 3. Effective Debye temperature for the Debye–Waller factor of Ni as a function of temperature. The effect of thermal expansion on the Birgeneau *et al.* fourth nearest neighbor model was obtained from the approximate relation $\Delta\theta^M/\theta^M = -\gamma\Delta V/V$ with $\gamma = 2$. The circles represent the experimental values.

able for a mathematically simplified force model[22]. It is of interest that at high temperature the temperature dependence of $\theta^M(T)$ as given by the first neighbor Begbie–Born model is in close agreement with experiment, as seen in Fig. 3. However, due to experimental scatter, the temperature dependence of $\theta^M(T)$ given by the thermal expansion effect alone cannot be ruled out.

Recently, Gilat and Nicklow[23] have introduced the parameter

$$\bar{\gamma}_n = -\frac{V}{\theta_D(n)}\frac{\Delta\theta_D(n)^*}{\Delta V}$$

where the Δ operator takes the difference in the quantity between two temperatures (we used 100° and 500°K). The plot of $\bar{\gamma}_n$ vs. n for Ni is shown in Fig. 4. The results are similar to those of Gilat and Nicklow who studied force models based on neutron data quantity $\bar{\gamma}_n$ is a monatonically decreasing for aluminum at different temperatures. The function of n and has values close to the value of the thermodynamic Gruneisen parameter for large n. As noted for aluminum[23] the relatively large fractional changes of the transverse mode frequencies as compared to the fractional changes of the longitudinal mode frequencies appears to be important in determining the shape of the γ_n vs. n curve. However, we have found that in some directions the fractional change in frequency for a particular polarization depends strongly on the wave length, and we intend to study the model dependence of the $\bar{\gamma}_n$ vs. n curve. Finally it is pointed out that experimental and theoretical studies of the lattice dynamics of Ni at various temperatures are being carried out for temperatures greater than those considered in this paper[24]*.

*Analogous to the parameter $\gamma_D(n) \equiv \dfrac{-\partial \ln \theta_D(n)}{\partial \ln V}$

*I am grateful to Dr. Earl F. Skelton for bringing this work to my attention.

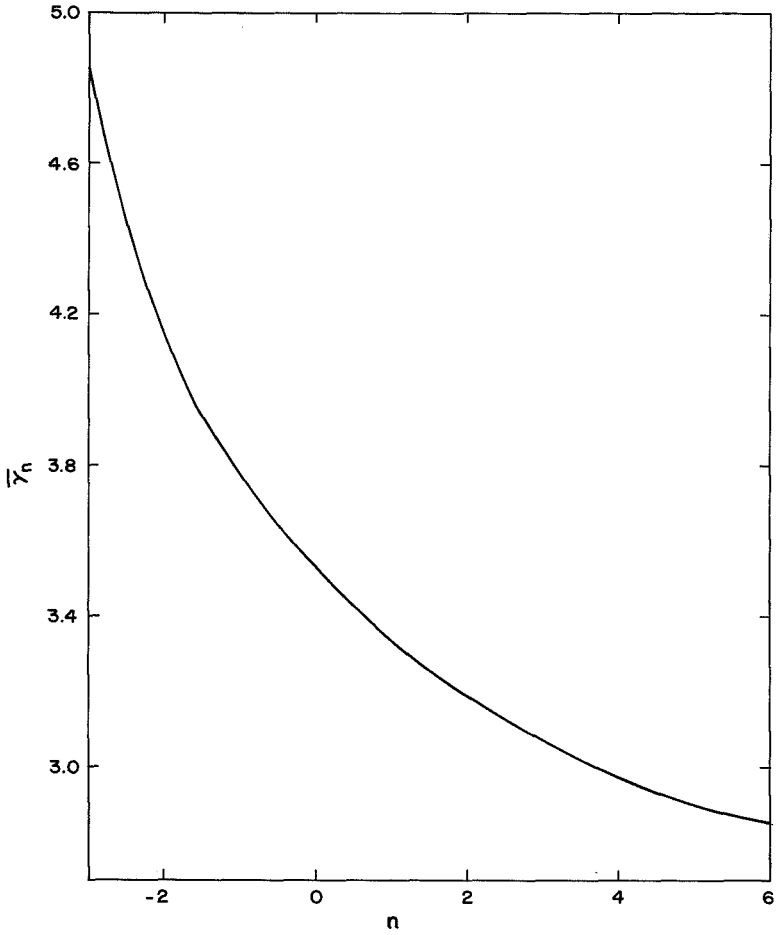

Fig. 4. A plot of $\bar{\gamma}_n \equiv -\frac{\Delta\theta_D(n)}{\theta_D(n)}\frac{V}{\Delta V}$ vs. n, where the Δ operator takes the difference in the quantity between $T = 100°$ and $T = 500°$K.

Acknowledgements—I wish to thank Anita Skelton and Dr. Earl F. Skelton for writing some of the computer programs. I also wish to thank Professor J. L. Katz and Dr. M. L. Klein for helpful conversations.

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